
Patent Office

12 A For scrutiny

11 8902092

Holland

19 NL

54 Material on the basis of a polyphenylene ether provided with polymerizable end groups.

51 Int.Cl⁵.: C08G65/48, C08J5/18, H05K1/03.

71 Applicant: General Electric Company, Schenectady, New York, U.S.A.

**74 Inventor: Mr.Ir. F. Grever
Postbus 117
4600 AC Bergen op Zoom.**

21 Application No. 8902092.

22 Submitted on 18 August 1989.

32

43 Scrutinized on 18 March 1991.

The document appended to this page is a print of the originally submitted description with claim(s) and drawing (s), if any.

General Electric Coopany, Schenectady, New York, United States of America

The applicant names the following as inventors: R.W. Avakian, Ch. Bailly, P. Eijsbouts, H. Ingelbrecht and I. Mamalis.

Material on the basis of a polyphenylene ether provided with polymerizable end groups.

Polyphenylene ethers have many well-known valuable properties, such as high softening temperature, low dielectric loss factor and a good ductility. However, their resistance to solvents leaves much to desire. This makes it difficult to employ polyphenylene ethers in printed circuit boards, because the plate must often be dipped into a cleaning bath of chlorinated solvent before the required lamination with copper. It is therefore desirable to provide a modified polyphenylene ether, that, on the one hand, retains its favourable properties and, on the other hand, possesses a better resistance against solvents.

Here "polyphenylene ethers" means not only polymers as described in, for example, US patent nos. 3,306,874 and 3,306,875 of Allan S. Hay or US patent nos. 3,257,357 and 3,257,358 of Gelu Stoeff Stamatoff, but also the copolymers formed predominantly out of phenylene ether units.

It is well-known to subject polyphenylene ethers to further reaction after their preparation. EP-A-54140 describes the preparation of a polyphenylene ether, which is substituted by a group, which is easily available for depolymerization, especially an isopropyl group. Subsequently styrene or methyl methacrylate can be polymerized with the formation of a graft copolymer. The terminal hydroxyl groups of the polyphenylene ether are however not obtained here. According to EP-B-172516, graft copolymers are similarly obtained, if polyphenylene ether is used as the grafting monomer and the principal chain is a copolymer of a styrene and an acrylonitrile. In the typical case, the polyphenylene ether is always less than 50% of the total polymer by weight. Here the

polyphenylene ether is bonded to a methyl chloride group of the copolymer or first converted with a chloromethyl styrene derivative, after which the polyphenylene ether provided with an end group is copolymerized in this manner with the nitrile monomer. Thus in both the cases a graft copolymer is obtained. In practice, polyphenylene ether is indeed provided with end groups with the help of trimellitic acid anhydride. Bonding of the polyphenylene ether is not possible here.

The invention is based on the conception that when the polyphenylene ether is provided with an end group derived from an unsaturated acid of the acrylic acid series, the product provided with the end group still possesses practically unchanged properties, but a polymerization reaction begins by heating, which causes chain lengthening, branching and/or bonding, by which the desired resistance against solvent is obtained.

The invention therefore refers to a material obtained on the basis of a polyphenylene ether provided with polymerizable end groups, which has the characteristic, that the bondable end group is a radical of a possibly substituted acrylic acid.

The other properties of the polyphenylene ether, which make this so suitable for printed circuit boards are retained by the introduction of end groups and the polymerization.

The introduction of the acrylic radical or the substituted acrylic radical in the terminal hydroxyl groups of the polyphenylene ether can be done, if necessary, by the acid itself, but is done, preferably, with one of its reactive derivative, especially the acid chloride. Here the simplest compounds of this series, namely acryloyl chloride and methacryloyl chloride, are specially preferable, thus the end group is preferably a radical of acrylic- or methacrylic acid.

A usual forming operation at high temperature, e.g., moulding or extruding, induces the further reaction and makes the product resistant to solvent. On the other hand it

is also possible to mould the product provided with end groups from a solution up to a film and subsequently harden the film at moderate temperature, typically, with the help of peroxides or UV-radiation. Here a very tough, but still stretchable film with high molecular weight, is obtained, which cannot be obtained by any other method.

It is also observed, that the material of the invention can contain additionally one or more usual additives for similar materials, such as fillers, reinforcement fibres, stabilizers, pigments and colorants, softeners, amorphous additives, additives for the improvement of the impact strength and fire-retardant additives.

The examples mentioned below illustrate the invention.

Example 1

Introduction of end groups

A double-walled glass reactor of 1 liter capacity is used, which is heated to 80° C and continuously stirred.

In the reactor, 500 g of a solution of 30% of polyphenylene ether by weight (hereinafter abbreviated as PPE) is introduced into toluene. First 8.7 g of dimethylbutylamine is added to this solution and mixed well with the solution. After that 6.8 g of methacryloyl chloride is added.

The mixture is stirred for 2 hours in order to bring the reaction to completion. The reaction is complete, if the indication of the OH-group measured with infrared spectroscopy, that originally amounts to 700-800 ppm in representative cases, is reduced to less than 50 ppm. The PPE so provided with end groups is isolated by precipitation with an anti-solvent, preferably methanol, then elutriated in clean anti-solvent and dried at 120° C under reduced pressure.

The intrinsic viscosity of the polymer provided with end groups is not changed with reference to the initial product within the measuring accuracy. A typical value for both the initial product as well as the product with end groups is 0.43 dl/g.

Example 2

Samples of the PPE provided with methacryloyl-end groups were heated for different times in a press. The molecular weight (MW) and the intrinsic viscosity (IV) of each sample were determined in chloroform. The results are presented in the table mentioned below.

Tabel A

| Dwell time in the press, minutes | Temperature, 300°C | | Temp. 320°C | |
|-------------------------------------|--------------------|----------|-------------|----------|
| | MW | IV(ml/g) | MW | IV(ml/g) |
| 0 | 41000 | 42.7 | 41000 | 42.7 |
| 2 | 99000 | 78.2 | - | - |
| 4 | 119000 | 98.4 | 134000 | 99.1 |
| 6 | 134000 | 105.6 | - | - |
| 10 | 137000 | 104.2 | (*) | (*) |

(*) not completely soluble

As reference, a PPE not provided with end groups was used. The IV of the unpressed powder was 44.7 ml/g and after the forming operation in the press the IV was 54.2 ml/g, a slight IV-increase than the normal in the press.

Example 3

Experiments were carried out with different PPE-samples corresponding to the dissolution in trichloroethane.

The results have been presented below in a table:

Table B

| Sample | Time up to visible dissolution, min |
|---|-------------------------------------|
| PPE after injection moulding | 1 |
| PPE filled with 30 % glass fibres | |
| according to Radlite process a) | 1 |
| PPE provided with methacrylate-end groups | |
| after heating: | |
| 4 minutes to 300° C | 2 |
| 6 minutes to 300° C | 5.5 |
| 10 minutes to 300° C | > 10 |
| 4 minutes to 320° C | > 15 |

a) A dispersion of PPE in glass fibres is applied and pressed at high temperature.

The above-mentioned results show, that while a high percentage glass fibres does not have any influence on the time duration until visible dissolution of the PPE takes place, the introduction of the end groups according to the invention has a remarkable effect in this respect.

CLAIMS:

1. Material on the basis of a polyphenylene ether provided with polymerizable end groups, with the feature, that the polymerizable end group is a radical of a possibly substituted acrylic acid.

2. Polyphenylene ether provided with polymerizable end groups according to claim 1, characterized by the fact, that the end group is a radical of acrylic or methacrylic acid.
3. Objects, especially printed circuit boards and films, prepared by using a material according to claim 1 of 2.
4. Procedure for the preparation of a polyphenylene ether provided with polymerizable end groups according to claim 1 or 2, characterized by the fact, that the terminal phenolic hydroxyl groups of the polyphenylene ether is converted into phenolate groups and the obtained product is allowed to react with a possibly substituted acrylic acid or with its reactive derivative.
5. Procedure according to claim 4, characterized by the fact, that (meth)acryloyl chloride is chosen as reactive derivative.
6. Procedure for the preparation of moulding parts from polyphenylene ether with increased resistance against solvent, characterized by the fact, that a polyphenylene ether provided with end groups according to claim 1 of 2 is subjected to a forming operation under heat and pressure.
7. Procedure for the preparation of films from polyphenylene ether with increased resistance against solvent, characterized by the fact, that a polyphenylene ether provided with end groups according to claim 1 of 2 is moulded from a solution to a film and the film is then polymerized further with the help of a peroxide catalyst or active radiation.